AD 430515

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

CAMERON STATION, ALEXANDRIA, VIRGINIA

64-9

ERR-FW-221
15 January 1964

HYDROTHERMAL SYNTHESIS OF R_2SiO_4 COMPOUNDS

Published and distributed under Contract No. AF33(657)-11214, Air Force Materials Laboratory Aeronautical Systems Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio.

GENERAL DYNAMICS | FORT WORTH

GDIIIIIIID

ERR-FW-221
Pure Science

HYDROTHERMAL SYNTHESIS OF R_2SiO_4 COMPOUNDS

Arthur J. Ehlmann
Department of Geology
Texas Christian University
Fort Worth 29, Texas

1 September 1963

RESEARCH & ENGINEERING DEPARTMENTS

This work was accomplished under Purchase Order No. 884899-8, a portion of the company-sponsored research program 414-63-518.

GENERAL DYNAMICS | FORT WORTH

INTRODUCTION

The mineral synthesis research contract at Texas Christian University has evolved into two essentially different studies: first, ferrites and the effects of ultrahigh pressure treatment[1]; second, hydrothermal synthesis of R_2SiO_4 (olivine-type) minerals. The second study was instigated to fill time gaps in the ferrite progress.

HYDROTHERMAL SYNTHESIS OF R_2SiO_4 COMPOUNDS

The pressure system for the hydrothermal synthesis equipment was completed on 3 August and the synthesis of olivine group minerals was begun immediately. The olivines are neosilicates with an ideal chemical formula of R_2SiO_4, where R can be Mg^{+2}, Fe^{+2}, Mn^{+2}, Ca^{+2}, and other divalent metals. The olivine structure consists of individual SiO_4 tetrahedra bound together by the divalent cations.

1. The ferrite project is reviewed in ARR-4, Research Summary Applied Research Program, January - June 1963, General Dynamics/Fort Worth, Texas, 1963. Subsequent work has been concerned with the effects of a "30 kb - 600°C" treatment; however, the samples have not all been "squeezed" at this time.

The Forsterite-Fayalite Series

The forsterite-fayalite series is a complete solid solution series between Mg_2SiO_4 (forsterite) and Fe_2SiO_4 (fayalite). Magnesium and ferrous iron substitute for each other in all proportions in the olivine crystal lattice. This series has been synthesized and the data presented in a master's thesis at Texas Christian University (Slaydon, 1961)[2]. The series has been resynthesized using the recently constructed equipment. The repetition of previous work provides a means of checking the efficiency and reliability of the new equipment.

Ten gram mixtures designed to give the following products were weighed out to one ten-thousandths of a gram: 100, 90, 75, 50, 25, and 10 mole percent forsterite. The starting materials were magnesium oxide, ferrous oxalate, and silicic acid. The magnesium oxide and the silicic acid were dried at approximately 1000°C for 24 hours. The ferrous oxalate was dried at approximately 150°C for 24 hours. The mixtures were ground in a small ball mill for one hour; the walls of the mill were then scraped as clean as possible, and the mixtures were ground for another hour. Approximately 0.25 gram of a mixture and 0.03 cc of distilled water were sealed in fine silver tubing by means of an acetylene torch.

2. Robert E. Slaydon, Jr., Hydrothermal Synthesis and Analysis of Some Olivine Group Minerals, Master's Thesis, Texas Christian University (1961).

The silver capsule was weighed on an analytical balance, placed in the pressure vessel, and brought to the desired temperature and pressure. At the end of the run the temperature was lowered, and the pressure was released. The silver capsule was removed from the pressure vessel and weighed to check for leakage. A summary of each run is shown in Table 1.

The products were analyzed with a Phillips Norelco diffractometer using CuKα radiation. The products of each run were scanned first at $2^{\circ} 2\Theta$ to determine the phases present. At least three scans at $1/4^{\circ}$ 2Θ per minute were made across the (130) peak, which occurs at approximately 32° 2Θ. Using the Bragg equation

$$n\lambda = 2d\sin\Theta$$

where $n\lambda = 1.5418$ A, the d(130) spacings were calculated from the values of 2Θ given in Table 2. The accuracy of the goniometer was checked against an external standard of silicon. The goniometer was found to be in error by 0.006° 2Θ. This is less than the accuracy with which the diffraction patterns can be read at $1/4^{\circ}$ per minute, the scan speed used. For this reason the values obtained on the three scans required no correction.

The values of the X-ray data for the 14 runs shown in Table 2 were used to derive the determinative curve shown in Figure 1. The statistical method used to derive the curve is shown in the appendix. On the same graph is shown a curve derived by Slaydon (1961) for the determination of the

Table 1 SUMMARY OF SYNTHESIS RUNS ON FORSTERITE - FAYALITE SOLID SOLUTION SERIES

Number	Comp. Mol% Fo	Wt. Capsule Before Run	Wt. Capsule After Run	T^oC	Pressure psi	Time Hrs.	Prod.
0-1	100	2.2117 gm	1.4393 gm	500	5000	2.5	Fo
0-2	100	?	?	500	5000	7	Fo
0-3	90	?	?	500	10000	4	Ss.
0-4	90	1.4315 gm	1.6097 gm	500	10000	7	Ss.
0-6	75	1.3935 gm	2.0675 gm	500	10000	4	Ss.+$MgCO_3$
0-7	75	1.0137 gm	1.0147 gm	500	10000	7	Ss.
0-8	50	0.9702 gm	1.2550 gm	500	10000	6	Ss.
0-10*	0-6	0.8574 gm	0.8580 gm	500	10000	8	Ss.
0-11	50	1.3581 gm	1.1975 gm	500	8000	6	Ss.
0-9	25	1.0227 gm	1.0495 gm	500	10000	24	Ss.
0-12	25	0.9798 gm	0.9390 gm	500	10000	24	Ss.
0-13	10	1.5385 gm	?	500	10000	8	Ss.
0-14	10	0.9927 gm	0.9686 gm	500	10000	7	Ss.
0-15	0	1.7194 gm	1.5370 gm	500	10000	8	Fa.
0-16	0	1.0011 gm	0.9633 gm	500	10000	8	Fa.

Fo = Forsterite
Fa = Fayalite
Ss. = Forsterite-Fayalite solid solution

*The starting materials for this run were part of the products of 0-6.

Table 2 DATA REVIEW FOR DETERMINING THE "d" SPACING OF THE (130) PLANE IN THE FORSTERITE-FAYALITE SOLID SOLUTION SERIES

Synthetic Number	Composition Mol% Fo	$^{o}2\theta$ Readings	Average 2θ	d(130)
0-1	100	32.312 32.300 32.338	32.316	2.770
0-2	100	32.302 32.303 32.338	32.314	2.770
0-3	90	32.325 32.325 32.275	32.308	2.771
0-4	90	32.287 32.280 32.290	32.286	2.772
0-7	75	32.163 32.162 32.175	32.167	2.783
0-10	75	32.175 32.187 32.175	32.179	2.782
0-8	50	32.000 31.950 31.975	31.975	2.799
0-11	50	32.000 32.000 32.000	32.000	2.797
0-9	25	31.800 31.775 31.837	31.804	2.814
0-12	25	31.825 31.838 31.862	31.842	2.809

Table 2 (Continued)

Synthetic Number	Composition Mol% Fo	$^{o}2\theta$ Readings	Average 2θ	d(130)
0-13	10	31.763 31.725 31.737	31.742	2.819
0-14	10	31.725 31.750 31.738	31.738	2.822
0-15	0	31.750 31.750 31.638 31.775 31.700 31.800 31.700	31.730	2.820
0-16	0	31.638 31.637 31.637	31.637	2.828

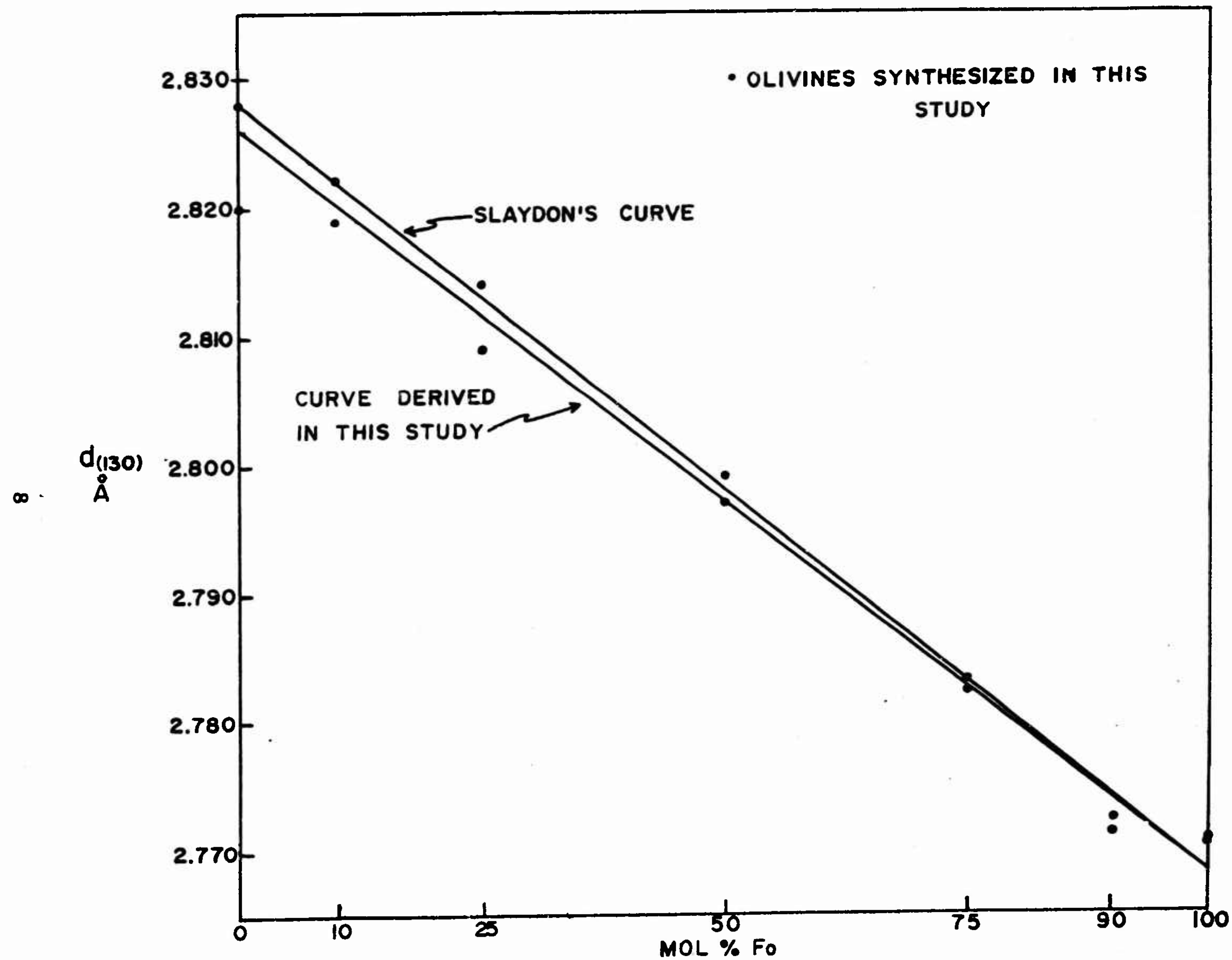

FIG. 1: DETERMINATIVE CURVES FOR SYNTHETIC OLIVINES

composition of synthetic olivines. This curve is based on 17 synthetic olivines.

The equation of the curve derived in the present study is

$$\text{Mol\% Fo} = 4895.91 - 1732.63\ d(130).$$

The correlation coefficient (r) for this curve is 0.9937. The fictive end points for this curve are

$$2.826\ d(130) = 0 \text{ mol\% Fo and}$$

$$2.768\ d(130) = 100 \text{ mol\% Fo.}$$

The equation for Slaydon's curve is

$$\text{Mol\% Fo} = 4708.94 - 1665.27\ d(130).$$

The correlation coefficient for Slaydon's curve is

$$r = 0.9965.$$

The fictive end points for Slaydon's curve are

$$2.828\ d(130) = 0 \text{ mol\% Fo and}$$

$$2.768\ d(130) = 100 \text{ mol\% Fo.}$$

Appendix

The following equation was used to derive the equation for the analytical curve for synthetic olivines in this report (Ferguson, 1959)[3]:

$$\overline{X} = \frac{\Sigma X - \dfrac{\Sigma XY - \Sigma X \Sigma Y/N}{\Sigma Y^2 - (\Sigma Y)^2/N}(\Sigma Y)}{N} + \frac{\Sigma XY - \Sigma X \Sigma Y/N}{\Sigma Y^2 - (\Sigma Y)^2/N} \quad Y$$

The following equation was used to determine the correlation coefficient (r) for the analytical curve (Ferguson, 1959):

$$r = \frac{N\Sigma XY - \Sigma X \Sigma Y}{\left\{\left[N\Sigma X^2 - (\Sigma X)^2\right] \quad \left[N\Sigma Y^2 - (\Sigma Y)^2\right]\right\}^{1/2}}$$

Where X = Mol% Fo predicted by d(130) spacing

X = Mol% Fo in each sample

Y = d(130) spacing

N = Number of samples

The following is a summary of the data from Table 2 used in the derivations of the analytical curve:

1. $\Sigma Y = 39.156$
2. $\Sigma X = 700$
3. $\Sigma Y^2 = 109.519954$
4. $\Sigma X^2 = 53900$
5. $\Sigma XY = 1947.030$

3. George A. Ferguson, <u>Statistical Analysis in Psychology and Education</u>, McGraw-Hill Book Co., Inc., New York, 1959, 347 pp.